Supporting Information

Investigation on the Catalytic Behavior of one Novel Thulium-Organic Framework with Planar Tetranuclear {Tm$_4$} Cluster as Active Center for

5 # Chemical CO$_2$ Fixation

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Table S1. crystallographic data and refinement parameters of NUC-37.

Complex	NUC-37
Formula	$C_{72}H_{64}N_7O_{35}Tm_4$
Mr	2263.02
Crystal system	hexagonal
Space group	$P6_3/mcm$
a (Å)	22.120(4)
b (Å)	22.120(4)
c (Å)	38.202(8)
α (°)	90
β (°)	90
γ (°)	120
V(Å^3)	16188(7)
Z	6
Dcalcd(g·cm^{-3})	1.393
μ(mm^{-1})	3.326
GOF	1.070
R_1 [I＞2σ(I)]^a	0.0379
wR_2 [I＞2σ(I)]^b	0.0969
R_1^a (all data)	0.0497
wR_2^b (all data)	0.1044
R_{int}	0.1094

$^a R_1 = \sum||F_o|-|F_c||/\sum|F_o|$. $^b wR_2 = [\sum w(|F_o|^2-|F_c|^2)]/\sum|w(F_o^2)^2|^{1/2}$

Table S2. selected bond lengths and angles of NUC-37.

Tm1-O1#1	2.228(4)	Tm1-O1#2	2.228(4)	Tm1-O3	2.202(4)
Tm1-O3#3	2.202(4)	Tm1-O5#5	2.292(6)	Tm1-O5#4	2.292(6)
Tm1-O1W	2.309(4)	Tm2-O2#1	2.323(4)	Tm2-O2#7	2.323(4)
Tm2-O4	2.272(4)	Tm2-O4#8	2.273(4)	Tm2-O1W#8	2.312(2)
Tm2-O1W	2.312(2)	Tm2-O6	2.326(6)	Tm2-O2W	2.552(8)
O1#1-Tm1-O1#2	86.6(2)	O1#2-Tm1-O5#4	115.9(2)	O1#1-Tm1-O5#4	81.7(2)
O1#1-Tm1-O5#3	115.9(2)	O1#2-Tm1-O5#3	81.7(2)	O1#2-Tm1-O1W	79.72(12)
O1#1-Tm1-O1W	79.72(12)	O3-Tm1-O1#2	89.76(17)	O3#5-Tm1-O1#1	89.76(17)
O3#5-Tm1-O1#2	162.04(15)	O3-Tm1-O1#1	162.04(15)	O3-Tm1-O3#5	88.3(2)
O3-Tm1-O5#3	80.8(2)	O3#5-Tm1-O5#3	115.5(2)	O3-Tm1-O5#4	115.5(2)
O3#5-Tm1-O5#4	80.8(2)	O3-Tm1-O1W	82.32(14)	O3#5-Tm1-O1W	82.32(14)
O5#3-Tm1-O5#4	50.2(4)	O5#3-Tm1-O1W	154.89(18)	O5#4-Tm1-O1W	154.89(18)
O2#6-Tm2-O2#2	74.90(19)	O2#2-Tm2-O6	141.48(10)	O2#6-Tm2-O6	141.48(10)
O2#6-Tm2-O2W	70.5(2)	O2#2-Tm2-O2W	70.5(2)	O4-Tm2-O2#2	82.16(16)
O4#8-Tm2-O2#6	82.15(16)	O4#8-Tm2-O2#2	136.78(15)	O4-Tm2-O2#6	136.78(15)
O4#8-Tm2-O4	90.7(2)	O4#8-Tm2-O1W	147.83(16)	O4#8-Tm2-O1W#8	92.31(14)
O4-Tm2-O1W#8	147.82(16)	O4-Tm2-O1W	92.31(14)	O4-Tm2-O6	74.55(16)
O4#8-Tm2-O6	74.55(16)	O4-Tm2-O2W	67.43(19)	O4#8-Tm2-O2W	67.43(19)
O1W-Tm2-O2#2	75.30(13)	O1W#8-Tm2-O2#6	75.31(13)	O1W-Tm2-O2#6	115.80(15)
O1W#8-Tm2-O2#2	115.80(15)	O1W#8-Tm2-O1W	69.01(15)	O1W#8-Tm2-O6	75.44(16)
O1W-Tm2-O6	75.44(16)	O1W#8-Tm2-O2W	142.06(12)	O1W-Tm2-O2W	142.06(12)
O6-Tm2-O2W	124.6(3)				

Symmetry transformations used to generate equivalent atoms: #1: 2-X,1-X+Y,3/2-Z; #2: 1+Y,+X,+Z; #3: 1-Y,+X-Y,+Z; #4: 1+Y,1-X+Y,1-Z; #5: 1-Y,1-X,1-Z; #6: 2-X,1-X+Y,+Z; #7: +X,+Y,3/2-Z; #8: 1-Y,+X-Y,3/2-Z.

Table S3. Comparison of the catalytic activity of various MOFs for the cycloaddition reaction of CO_2 with styrene oxide.

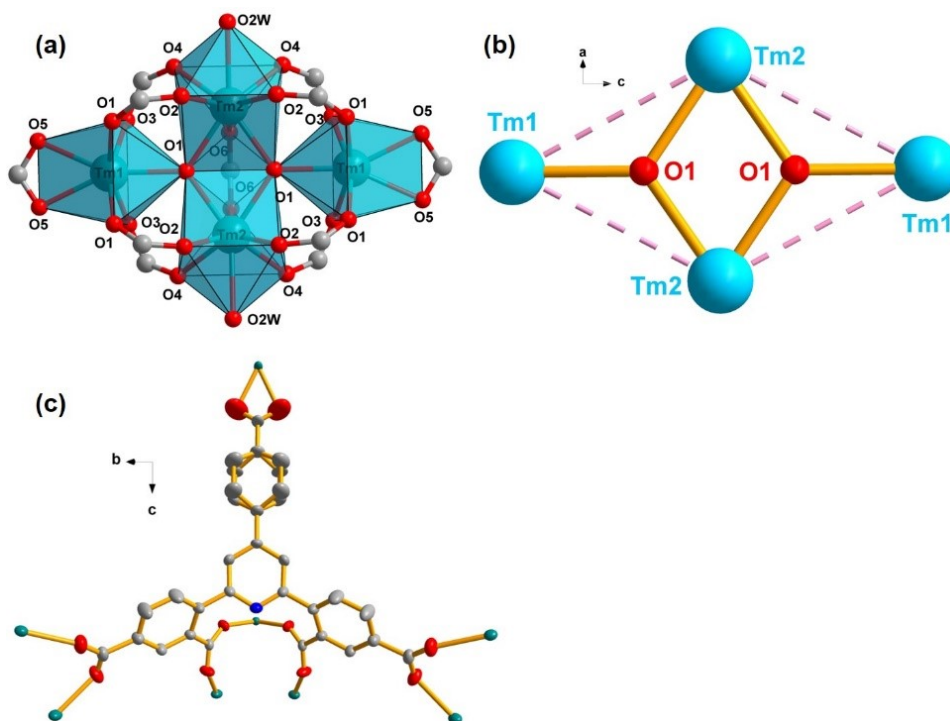| Catalyst	Catalyst (mol%)	Time (h)	Pressure (MPa)	Temp. (°C)	Yield (%)	Ref.
Rh-PMOF-1	0.2	24	0.1	100	88	S1
Zn-2PDC	0.49	3	1	80	89	S2
TCM-16 (Zr)	0.5	16	0.1	100	93	S3
$[Mn_5L(H_2O)_6 \cdot (DMA)_2]$	0.5	12	0.2	80	94	S4
JLU-MOF58 (Zr)	0.1	12	0.1	80	65	S5
$Co_6(TATAB)_4(DABCO)_3(H_2O)$	0.2	15	0.8	80	100	S6
$\{Ni(muco)(bpa)(2H_2O)\}$	0.5	12	0.8	80	81	S7
$ZnMOF-1-NH_2$	1	8	0.8	80	88	S8
$In_2(OH)(btc)(Hbtc)_{0.4}(L)_{0.6}$	0.51	4	2	80	73	S9
NUC-37a	0.5	5	0.1	75	98	this work

Figure S1. The coordination mode of tetranuclear {Tm$^{III}_4$} cluster (a); the thulium-hydroxide structure (b); the coordination mode of H$_5$BDCP ligand (containing disordered C atoms) (c).

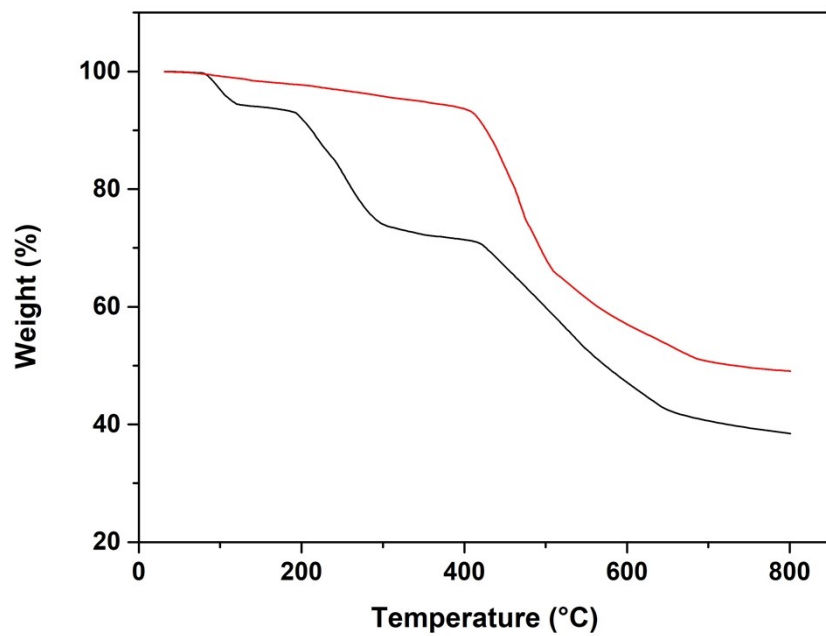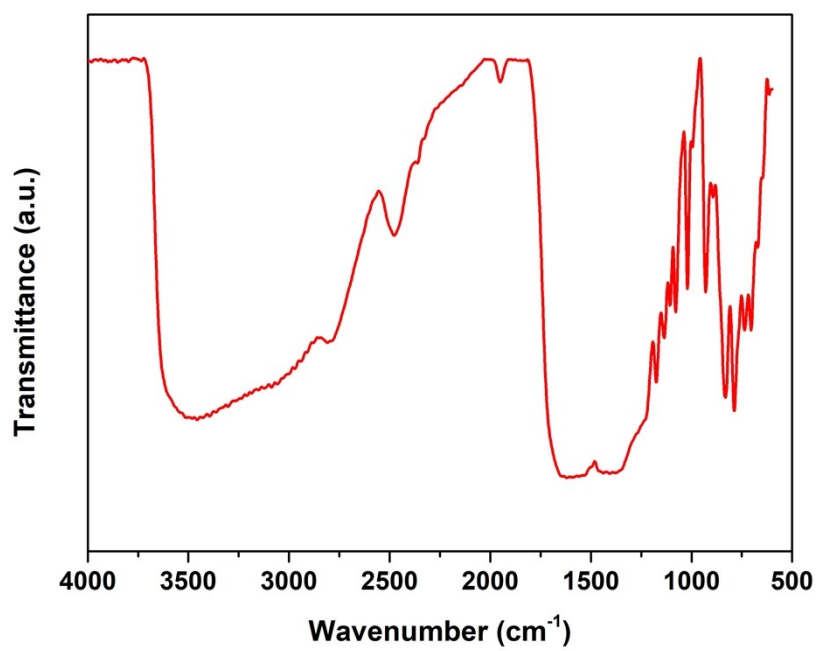**Figure S2. TGA curves of as-synthesized (black) and activated (red) sample of NUC-37.**

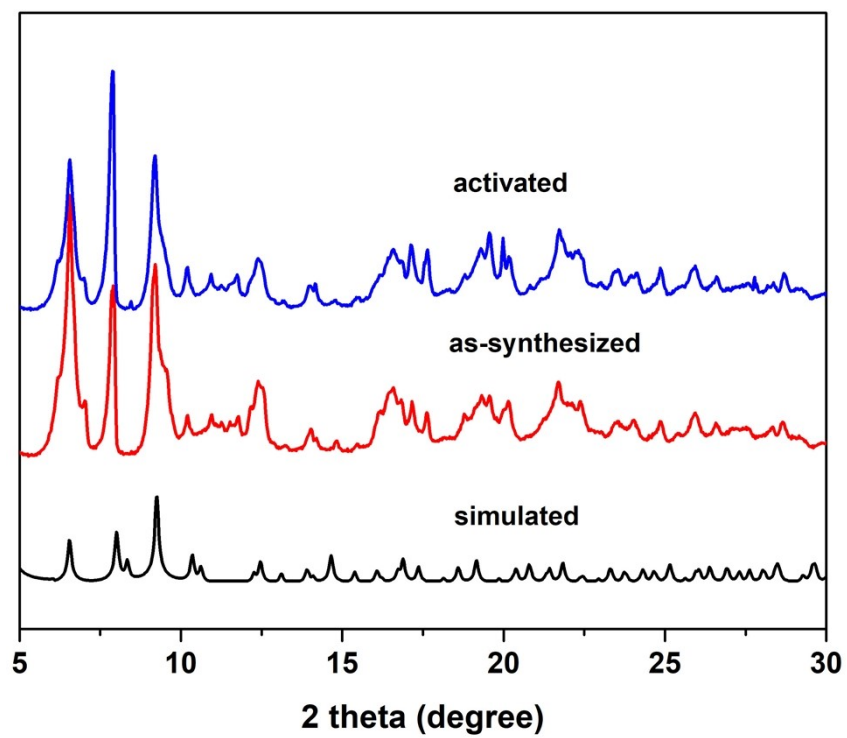**Figure S3. IR spectra of as-synthesized NUC-37.**

Figure S4. PXRD patterns of NUC-37 before and after activation.

Isosteric Heat Calculation.

The Q_{st} value is a parameter that describes the average enthalpy of adsorption for an adsorbing gas molecule at a specific surface coverage and is usually evaluated using two or more adsorption isotherms collected at similar temperatures. The zero-coverage isosteric heat of adsorption is evaluated by first fitting the temperature-dependent isotherm data to a virial-type expression, which can be written as:

$$lnP = lnN + \frac{1}{T}\sum_{i=0}^{m} a_i N^i + \sum_{i=0}^{n} b_i N^i \qquad (1)$$
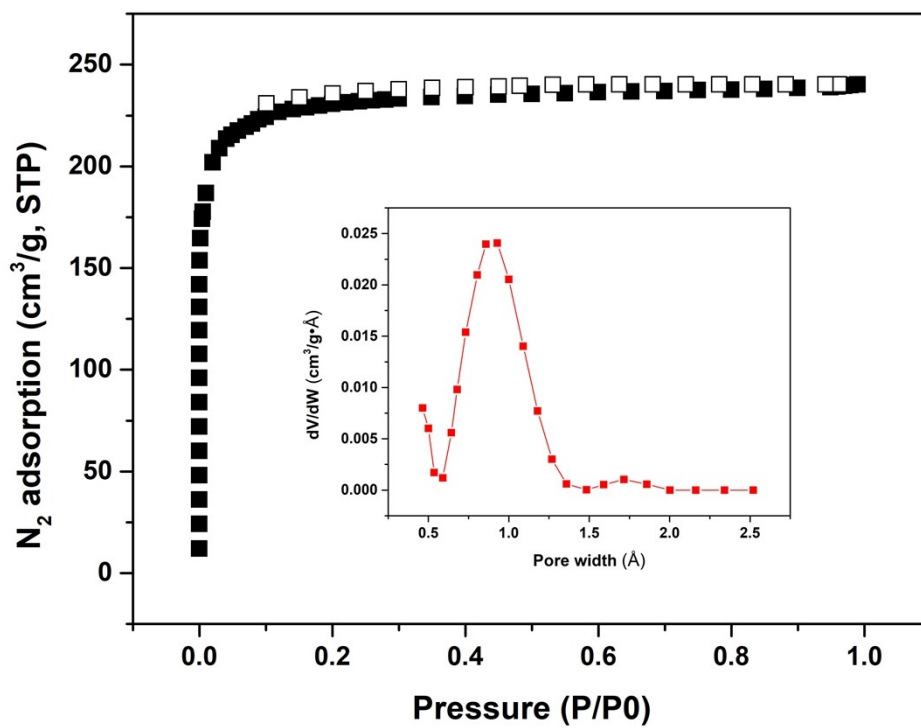
$$Q_{st} = -R \sum_{i=0}^{m} a_i N^i \qquad (2)$$

Figure S5. N$_2$ absorption and desorption isotherms of NUC-37a at 77 K (insert: the pore size distribution).
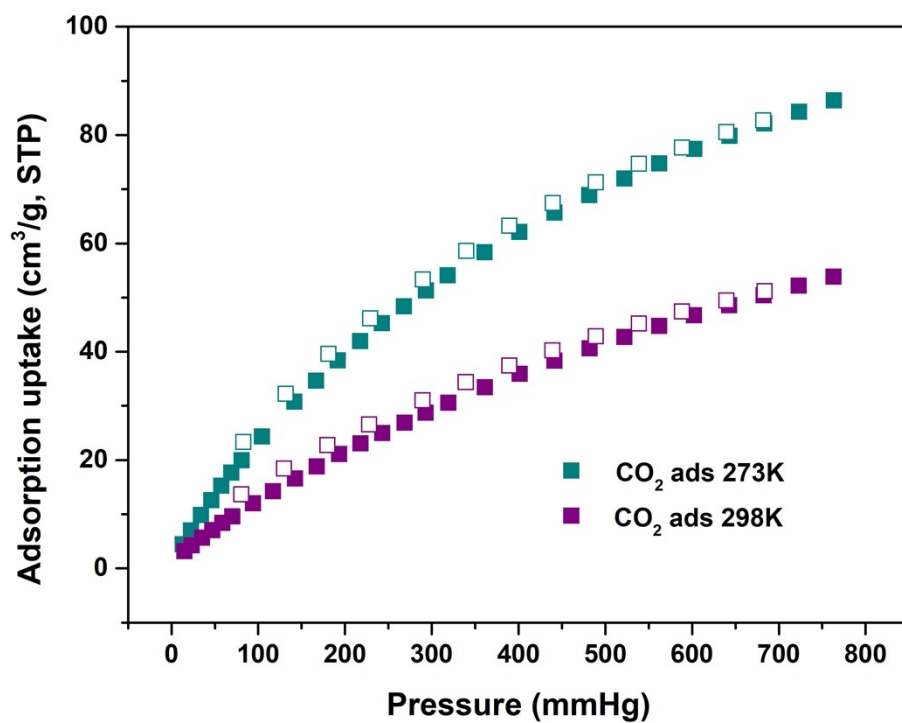
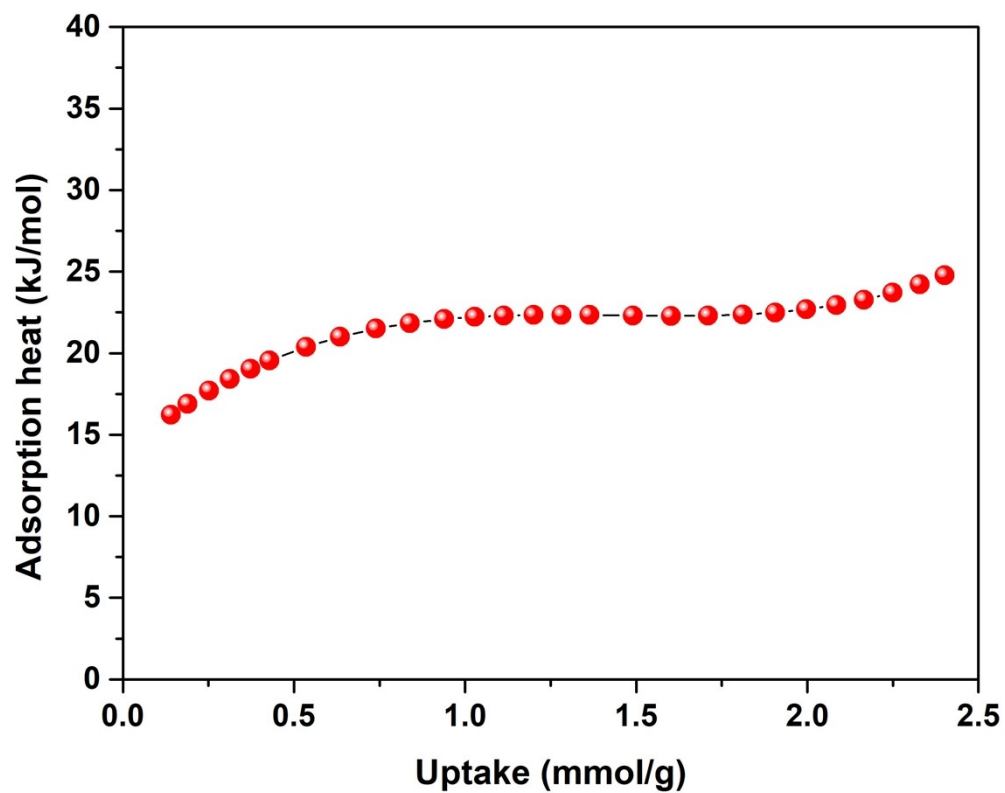**Figure S6.** Adsorption isotherm of CO_2 at 273K and 298K.

Figure S7. CO$_2$ adsorption heat calculated by the virial equation of NUC-37a.

Yield Calculation Based on the GC-MS Analysis

Gas chromatography mass spectrometry (GC-MS) analyses were performed on a time-of-flight Thermo Fisher Trace ISQ GC/MS instrument, the yield (%) was calculated based on the consumption of starting material using the equation:

$$Yield\ (\%) = \left(\frac{\frac{area\ of\ reactant\ at\ 0\ hour}{area\ of\ interal\ standard\ at\ 0\ hour} - \frac{area\ of\ reactant\ at\ any\ time}{area\ of\ interal\ standard\ at\ any\ time}}{\frac{area\ of\ reactant\ at\ 0\ hour}{area\ of\ interal\ standard\ at\ 0\ hour}} \right) \times 100\% \qquad (3)$$
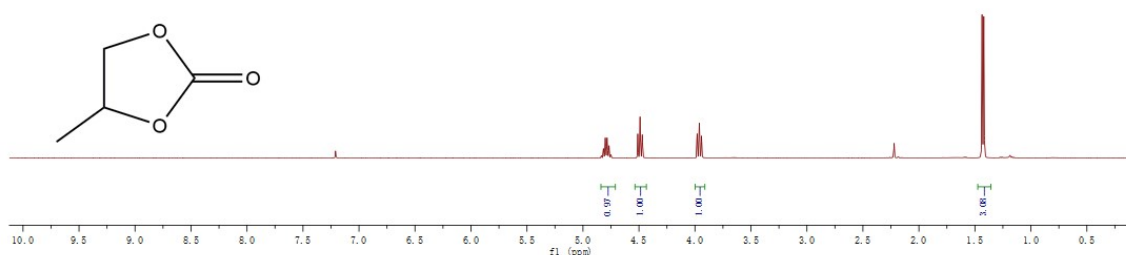
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Figure S8. The ^{1}H NMR spectrum of 4-methyl-1,3-dioxrum-2-one (Figure 3, entry 1).
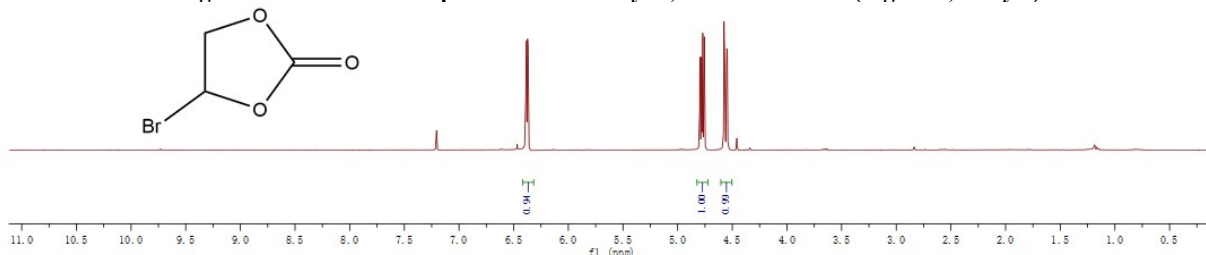

Figure S9. The ^{1}H NMR spectrum of 4-bromo-1,3-dioxolan-2-one (Figure 3, entry 2).
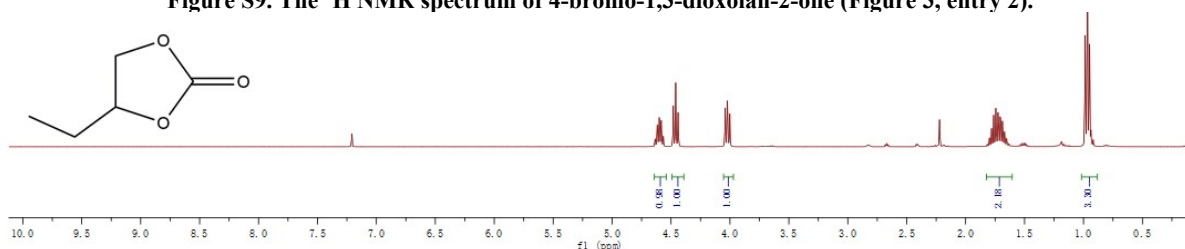
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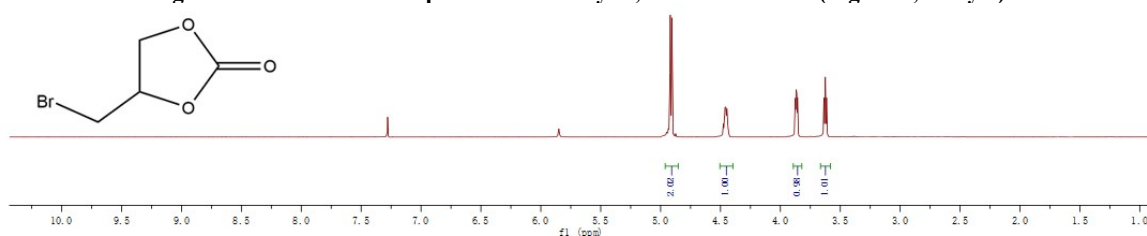**Figure S10.** The ^{1}H NMR spectrum of 4-ethyl-1,3-dioxolan-2-one (Figure 3, entry 3).

Figure S11. The ^{1}H NMR spectrum of 4-(bromomethyl)-1,3-dioxolan-2-one (Figure 3, entry 4).
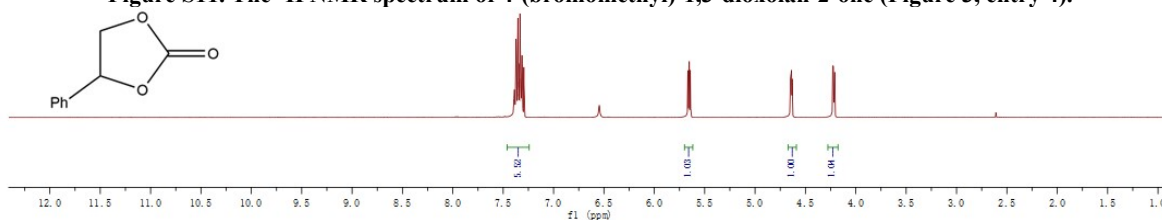

10   **Figure S12.** The ^{1}H NMR spectrum of 4-phenyl-1,3-dioxolan-2-one (Figure 3, entry 5).
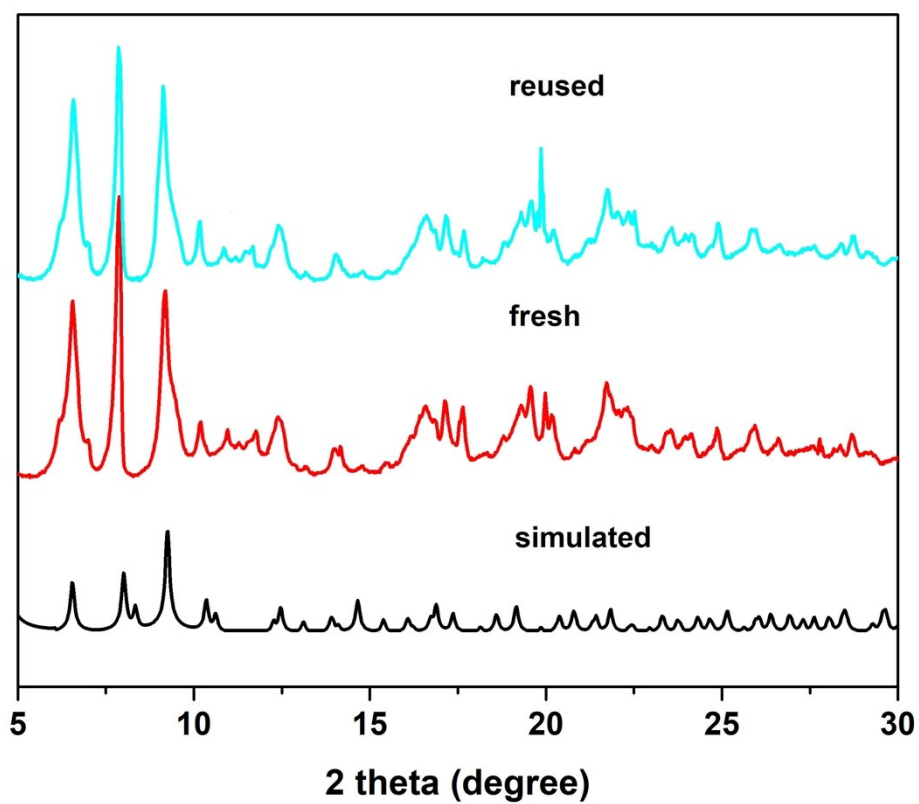
Figure S13. PXRD patterns of fresh and reused NUC-37a catalyst.
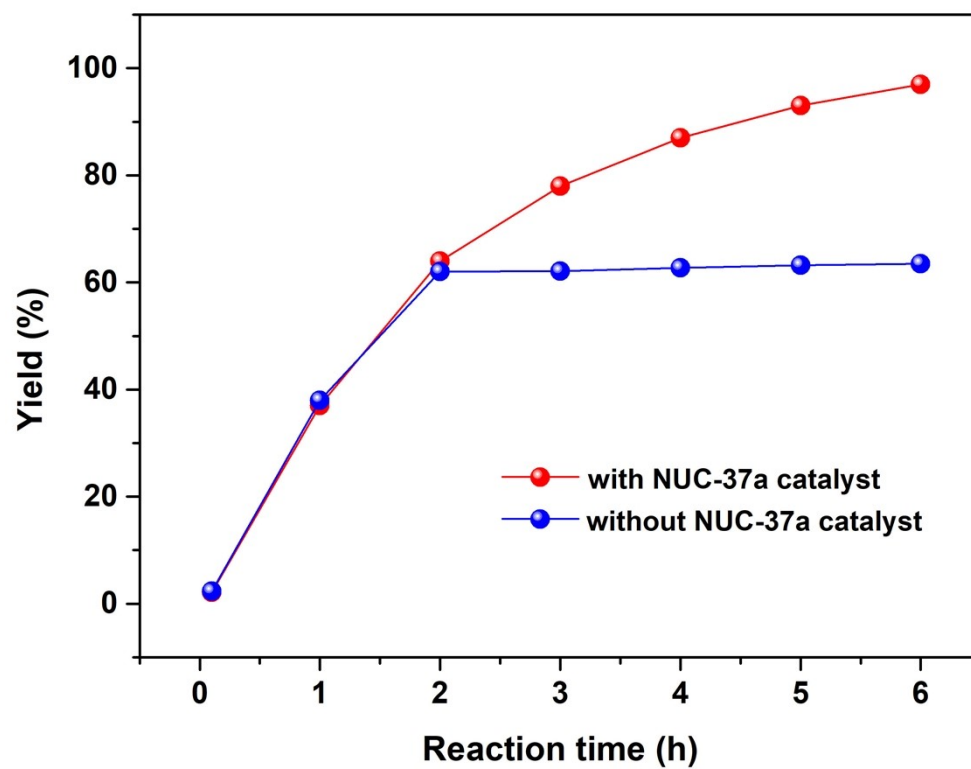
Figure S14. The hot filtration experiment of cycloaddition reaction catalysed by NUC-37a.

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Reference

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